What Is Oxidation In Lubricating Oil?

By MARK BARNES

When explaining what oxidation is, no one does it better than Mark Barnes from Noria Corp. We wanted to share his input from a past issue of POA Magazine.

Oxidation is perhaps the most common chemical reaction, not just in lubrication chemistry, but also in nature as a whole. Simply stated, oxidation is the chemical reaction of an oil molecule with oxygen, which is present from either ambient or entrained air. (In a strict chemical sense, oxidation does not necessarily need to involve oxygen, although for the purposes of this article, the discussion is confined to oxidation reactions involving oxygen.) Oil oxidation is no different than other commonly encountered oxidation reaction, such as rusting. Just like the effects rusting and other corrosive processes have on metal substrates, oil oxidations results in a catastrophic and permanent chemical change to the base oil molecules.

In the case of oil oxidation, the reaction results in the sequential addition of oxygen to the base oil molecules, to form a number of different chemicals species, including aldehydes, ketones, hydroperoxides and carboxylic acids.

The rate at which base oil molecules react with oxygen depends on a number of factors. Perhaps the most critical is temperature. Like many chemical reactions, oxidation rates increase exponentially with increasing temperature due to the Arrehenius rate rule. For most mineral oils, a general rule of thumb is that the rate of oxidation doubles for every 10°C (18°F) rise in temperature above 75°C (165°F). Because of this, synthetic oils are often required in high temperature applications to prevent rapid oil oxidation. But why are synthetic hydrocarbon oils (SHCs) more oxidatively stable than conventional minerals oils? After all, they're both comprised of carbon and hydrogen atoms joined together in similar paraffinic chains to refined mineral oils.

The answer to this question is two-fold. First, SHCs, and for that matter highly-refined mineral oils, have very few impurities. Some of the impurities, particularly aromatic compounds found in solvent refined mineral oils, are less stable than the paraffinic molecules that comprise the majority of molecules in SHCs and highly-refined mineral oils.

The Effects of Oxidation - What to Look for on an Oil Analysis Report
While controlling temperature and using higher-quality base oils can help limit the degree and rate of oxidation, the eventual breakdown of the base oil molecules due to oxidative processes is inevitable. One common feature of these reaction by-products is the carbon-oxygen double bonds, termed a carbonyl group. Carbonyl groups are noted for their characteristic absorption of infrared light in the 1740 cm-1 region. For this reason, Fourier transform infrared spectroscopy (FTIR), which measures the degree of infrared absorption in different parts of the infrared spectrum, can be an excellent tool for pinpointing base oil oxidation.

Perhaps the most noteworthy of the reaction by-products are the carboxylic acids. As the name implies, carboxylic acids are acidic in nature, just like other more common acids such as sulfuric and hydrochloric acids, although they are not nearly as strong.

Common household vinegar contains carboxylic acid - an acetic acid. Because oil oxidation results in the formation of carboxylic acids, it stands to reason that the acidity of an oil that has undergone appreciable oxidation will increase. As such, an Acid Number test, which uses a wet chemistry titration method to determine the concentration of acids present in an oil, can be used to determine the degree to which an oil has oxidized.

Care must be exercised when using Acid Number data to gauge oil oxidation because a number of additives - both new and degraded - can result in changes in an oil's Acid Number and can mask the real effects of base oil oxidation. Similarly, depending on the working environment, certain ingressed contaminants may also cause the acid number to change, masking the effects of oil oxidation. For this reason, the presence of a characteristic infra peak at 1740 cm-1 in the FTIR spectrum can be an instructive piece of confirmatory evidence when assessing oil oxidation.

While carboxylic acids by themselves are bad news and can cause acidic corrosion, an increase in acid number is usually a harbinger (forerunner) of an even more damaging chemical process - the formation of sludge and varnish. Sludge and varnish form when oxygenated reaction by-products, such as hydroperoxides and carboxylic acids, combine to form larger molecular species. When a number of such molecules combine, the process is termed polymerization and results in the formation of large molecules of high molecular weight.

Because the viscosity of an oil is directly related to the size of the molecules, any degree of polymerization will result in an increase in the measured viscosity. Allowed to progress too far, polymerization continues to such an extent that solid material - sludge and varnish - forms in the oil, as the molecules become too large to remain a liquid. This material is sticky and can cause filter plugging, fouling of critical oil clearances and valve stiction in hydraulics systems.

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